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X-RAY FLUORESCENCE DETERMINATION OF SULPHUR IN OILS
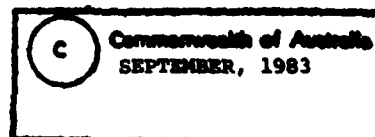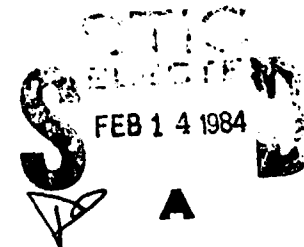
BY A THIN FILM METHOD

W.B. Searle*

* MATERIALS TESTING LABORATORY

SYDNEY, N S W

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ABSTRACT

A thin film dilution sample preparation technique for the determination of sulphur in petroleum products is described. An internal control standard compensates for variations in oil film thickness. The procedure utilises a mixture of sample and an alkyd resin to improve adhesion to a Mylar substrate and to reduce sample flow during irradiation. The method is quantitative and has good repeatability for sulphur contents up to 5%. Accuracy is comparable with that obtained by chemical methods. The detection limit for sulphur was estimated to be 0.03%.

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TITLE

X-RAY FLUORESCENCE DETERMINATION OF SULPHUR IN OILS BY A THIN
FILM METHOD

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	Petroleum Products
	Sulfur

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ABSTRACT

A thin film dilution sample preparation technique for the
determination of sulphur in petroleum products is described.   An internal
control standard compensates for variations in oil film thickness.   The
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CONTENTS

X-RAY FLUORESCENCE DETERMINATION OF SULPHUR IN

OILS BY A THIN FILM METHOD

1. INTRODUCTION

The quantitative x-ray fluorescence analysis of sulphur in hydrocarbons depends on the carbon to hydrogen ratio and is influenced by the presence of elements in the matrix such as barium, zinc, calcium, lead and chlorine. Elements in the matrix affect the linearity of the relationship between the analyte concentration and fluorescent radiation intensity. The analysis is further complicated by matrix itself, that is variation in the physical and chemical composition of the sample relative to the standard which affect the intensity of the analyte radiation. These various effects, including absorption and enhancement, must be corrected or compensated for.

Techniques for overcoming or minimising matrix effects include the use of direct comparison standard methods [1], internal standard procedures using scattered x-rays [2], addition of a suitable internal standard element [3], and standard addition and dilution techniques [4].

Toft [5] has stated that the method of ASTM D2622, Sulphur in Petroleum Products (X-Ray Spectrographic Method) suffers from two major disadvantages, viz.

(1) "Since it does not incorporate any correction for the absorption by the matrix of the emitted $SK\alpha$ radiation, the accuracy of the method will suffer if the total mass absorption coefficient for $SK\alpha$ radiation of the sample differs much from that of the standard", and

(2) "there is no correction for the absorption of $SK\alpha$ radiation by sulphur itself."

He adopted an internal lead standard to compensate for absorption and enhancement effects for sulphur contents up to 1.7% m/m.

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This note describes a method using a thin film of oil, in which the sulphur radiation is absorbed, and an internal control standard (zirconium or barium) to compensate mainly for variations in the thickness of the oil film. By incorporating an alkyd resin into the sample mixture the adhesion of the oil film to the Mylar sheet substrate is improved to the extent that the film does not flow during irradiation in the conventional inverted position. The method has now been successfully used for the determination of sulphur in fuel oils, lubricating oils and some oil additives.

2. EXPERIMENTAL

2.1 Reagents

Sulphur Additive : A commercial product containing 33% m/m sulphur.[*]

Sulphur Standards : NBS certified sulphur in residual fuel oil.

Internal Control Standards :

    Barium   : 12% m/m as barium "nonylphenate" in white spirit.[+]

    Zirconium : 8% m/m as zirconium "octoate" in white spirit.[+]

    Copper   : 5% m/m as copper naphthenate in a high boiling point solvent.[+]

Alkyd Resin Solution : Product P-671 (sulphur free) diluted 1:1 with white spirit.[+]

Organic Lead Solution : 24% m/m as lead "octoate" in white spirit.[+]

White Oil : Liquid paraffin (sulphur free).[++]

2.2 Apparatus

The measurements were carried out on a PW1540 manual spectrometer with a PW1010 generator. A helium path was provided for all of the determinations. The operating parameters are given in Table 1. The oil sample was drawn into a thin film on a 25 μm Mylar substrate using a wire-wound metering rod (K Hand Coater - K Bar No. 3).

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[*]   Lubrizol Aust. Pty Ltd.

[+]   A.C. Hatricks Chemicals Pty Ltd.

[++] Ajax Chemicals

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2.3 Sulphur Standards

Suitable quantities of the sulphur additive, or alternatively, 5.00 g of the certified sulphur in oil standards were accurately weighed so that the final concentration of sulphur was within the range of 0-5%. Where necessary white oil may be used as a diluent.

2.4 Preparation of Sample and Standard Films

Standards and samples were prepared similarly by weighing 5.00 g of the oil sample and 4.00 g of the internal control standard into a 25 ml capacity glass stoppered bottle. Approximately 10 ml of the alkyd resin mix were added and the contents thoroughly shaken to ensure homogeneity.

A portion of the final mixture was poured onto a supported Mylar sheet and drawn into a thin film using the K Hand Coater. A disc was cut from the central area of the film and mounted in the x-ray sample cup so that the oil layer would be closest to the x-ray target. Duplicates were prepared from each sample and the reproducibility of the intensity data, relative to a suitable external reference standard to compensate for instrumental drift, was noted.

2.5 Analytical Curves

The fluorescent radiation intensities of sulphur and zirconium were measured. Their ratio was calculated and plotted against the concentration of sulphur. A linear relationship over the 0-5% concentration range was obtained. For comparison purposes separate mixtures were prepared from the samples listed in Table 2 using copper and zirconium as control elements. The x-ray sample cup was filled and the ratio of the intensities obtained. The depth of the oil mixture in the sample cup for these determinations exceeded the critical thickness for the fluorescing radiations from both the sulphur and control element.

3. RESULTS

The nonlinear relationship obtained between analyte concentration and intensity showed that matrix effects were present in bulk solutions using copper as an internal control (Fig. 1). Matrix effects were reduced using zirconium as the control element (Fig. 2). When the mixtures were formed into a thin film matrix effects were negligible as evidenced by the linear relationship between the analyte intensity ratio and concentration (Fig. 3).

Interference effects of lead on the sulphur fluorescent radiation intensity were estimated by the addition of various amounts of lead octoate to a sample having a known sulphur content and recording the change in sulphur intensity. The results obtained on thin film specimens and thick solutions

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are illustrated in Fig. 4. Relatively small changes in the ratio of sulphur to barium intensity was found in the case of thin film specimens. Lead contents up to about 6% m/m may be tolerated in thin film specimens without a significant loss in accuracy for sulphur determinations when barium was used as the internal control element. The wet film thickness was approximately 24 μm and the results demonstrate that the films are thin enough in order for matrix effects to be significantly reduced or controlled by means of the internal standard.

The accuracy of the method was determined by comparing the results obtained on certified sulphur in oil samples obtained by ASTM D129 with those quantities found by the thin film procedure (Table 2). The agreement was satisfactory. The repeatability of the technique determined on ten different mixtures from one oil sample containing 3% m/m sulphur gave a coefficient of variation of 1.3%. The change in sulphur to control intensity ratio with time (approx. 6 hrs) was less than 0.5%.

A nominal value of 0.03% was calculated for the lower limit of detection using three standard deviations of the background level intensity measured on a "blank" at the analyte setting. In practice the smallest quantity that can be measured reliably is about 0.05% and this is considered a reasonable lower limit.

4. CONCLUSIONS

The data presented in Table 2 illustrate a few applications of the method. Satisfactory agreement with chemical results was obtained. The technique could supplement conventional XRFS methods for sulphur determinations on contaminated oils which would otherwise involve numerical correction procedures or multiple sample preparations. Once standardisation has been carried out the analysis of sulphur in a hydrocarbon requires about 10 minutes employing only one sample preparation.

5. ACKNOWLEDGEMENT

I wish to thank W.R. Hindson for helpful comments and suggestions relating to the paper.

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T A B L E 1

Instrumental Operating Parameters

Instrumental Parameter	E L E M E N T			
	Sulphur	Barium	Zirconium	Copper
Analytical Line	Kα	Lα	Lα	Kα
Wavelength, Å	5.373	2.7752	6.0702	1.541
Analysing Crystal*	PE	LiF 200	PE	LiF 200
Angular Position, 2θ	75.50	87.14	89.05	45.00
X-ray Target	chromium	chromium	chromium	chromium
Detector	F1	F1	F1	F1
Collimation, μm	Coarse (480)	Fine (160)	Coarse (480)	Fine (160)
Tube Voltage, kV	50	50	50	50
Tube Current, mA	18	18	18	18
Path	helium	helium	helium	helium

* LiF : Lithium Fluoride

* PE : Pentaerythritol

F1 : Flow proportional counter
(using 10% methane in argon)

T A B L E   2

Comparison of sulphur determinations by x-ray and chemical methods

Type of Sample	Sulphur, % m/m	
Fuel Oils	X-ray	Chemical
A	0.72	0.80
B	2.10	2.14
C	3.02	3.09
D	4.23	4.27
NBS 1621	1.08	1.05
NBS 1622	2.26	2.14
NBS 1624	0.26	0.21
Lubricating Oils		
E	0.56	0.65
F	1.18	1.20
G	1.22	1.25
Oil Additives		
H (containing 3.3% Ba, 3.5% Ca)	2.25	2.1*
I (containing 7.1% Ba, 1.3% Zn, 1.3% P)	2.84	2.7*
J (containing 4.6% Ba, 2.1% Zn, 2.1% P)	4.08	3.9*
K (containing 2.9% Zn, 2.6% P)	5.35	5.5*

* Values reported by manufacturer from one determination by
  ASTM D129.
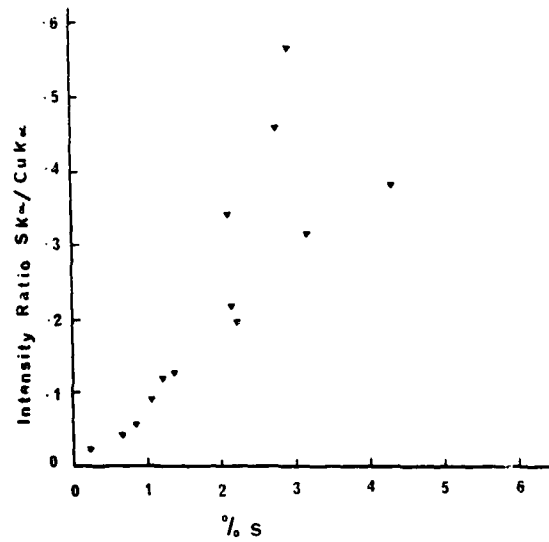
FIG. 1   Relation between the ratio of sulphur to copper
          fluorescent radiation intensity and
          concentration measured on bulk solutions.
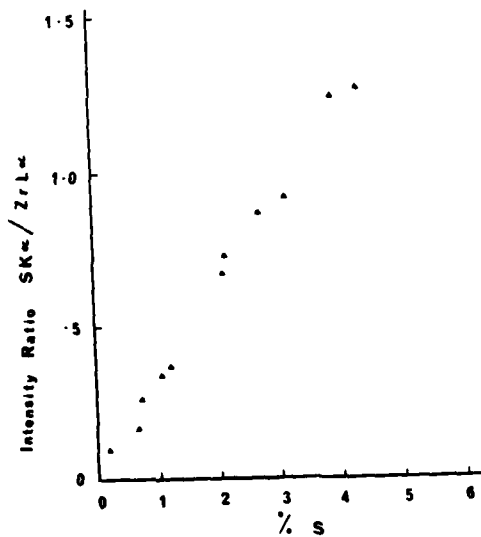
FIG. 2   Relation between the ratio of sulphur to zirconium
          fluorescent radiation intensity and concentration
          measured on bulk solutions.
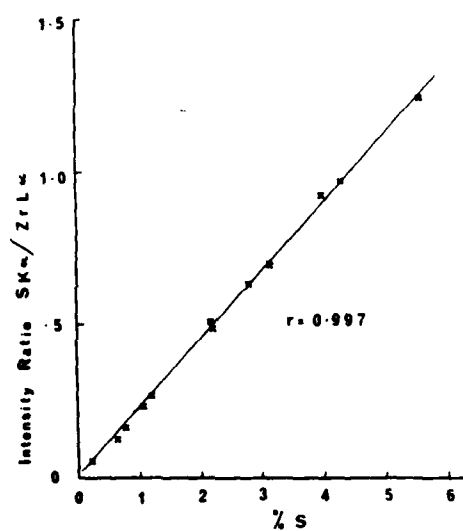
FIG. 3   Relation between the ratio of sulphur to zirconium
          fluorescent radiation intensity and concentration
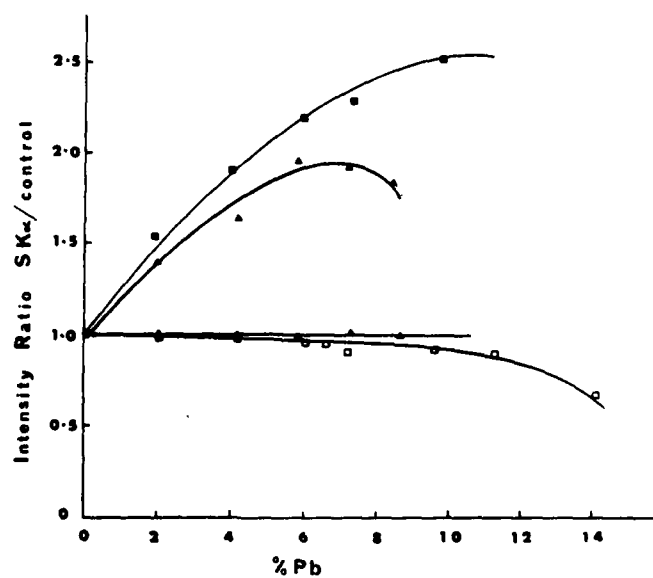   measured on a thin film specimen.

FIG. 4   Effect of lead addition on the ratio of sulphur
          to control fluorescent radiation.

■ bulk specimen, copper as a control.
▢ thin film specimen, copper as a control.
▲ bulk specimen, barium as a control
△ thin film specimen, barium as a control.

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